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Oxidative Quenching of Photoexcited Ru(II)-Bipyridine Complexes by Oxygen

Danielle Rebecca Latham
East Tennessee State University

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Danielle Latham and Dr. Yuriy Razskazovskiy

Department of Physics and Astronomy

East Tennessee State University

1. Introduction

1.1 Thermodynamics and Control of Photoinduced Electron Transfer

To make a change in a molecule, be it moving an electron, breaking a bond, or combining molecules, some amount of energy is required. In this case, a reduction reaction is in question. A reduction reaction is simply the moving of an electron. This type of reaction leaves the donor (the molecule that donates the electron) with an increased positive charge, and the acceptor (the molecule that accepts the electron) with an increased negative charge. [1] Different electron transfer reactions have standard reduction potentials which is a measure of a species ease of gaining electrons.

$$D^{+n} + ne^{-} \rightarrow D$$

$$A + ne^{-} \rightarrow A^{-n}$$

$$E^{o} = E_A - E_D$$

When viewed in the opposite direction, the standard reduction potential can be used to determine the difficulty of a species losing electron. In this generic example the donor is D, once again, and the acceptor is A. To compare the reactions, the donor reaction is read backwards, changing the sign of the potential. In our case, the donor is ruthenium (II) and the acceptor is oxygen. The potential values are in volts.

$$Ru^{3+} + e^- \leftrightarrow Ru^{2+} \ldots\ldots\ldots\ldots + 1.29V$$
$$O_{2(aq)} + e^- \leftrightarrow O_{2(aq)}^- \ldots\ldots\ldots\ldots - 0.33V$$

$$E^0 = -0.33V - (+1.29V) = -1.62V$$
$$\Delta G = -nFE^0 = -(1)\left(96.5\frac{kJ}{V * mol}\right)(-1.62V) = 98.1\frac{kJ}{mol}$$

The amount of energy it takes to transfer the electron is related to the Gibbs energy of the reaction. As a reaction occurs there is a change in the energy level between the reactions and products. The change in Gibbs energy can be determined in electron transfer reactions by measuring the standard potential of each part of the reaction. Reactions with a positive standard potential occur spontaneously. For the reaction in question, $Ru^{2+}+O_2 \rightarrow Ru^{3+}+O_2^-$, the standard potential is -1.62V. This highly negative value means the reaction is not going to proceed spontaneously under normal conditions. However, certain situations can arise which lower the energy required for a certain reaction to occur. By exciting Ru^{2+}, the electron that will be transferred is pushed to a higher energy level by moving it from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which means it requires less energy to be transferred or exchanged to the oxygen molecule. [2] This has been done bfore with serval other complexes with low oxidation potentials before. [3-5] This excitement for ruthenium(II) is done using a photon of wavelength 470 nm. This moves the the standard potential to a more positive number by including the energy from the photon. This is shown in the following equation where E_{00} is the excited state energy.

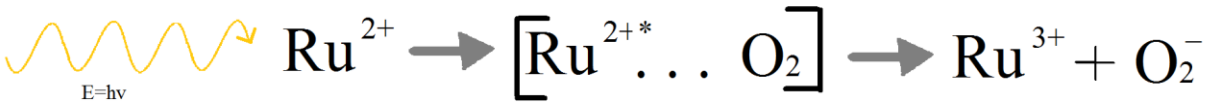
$$E^0 = E_A - E_D + E_{00}\ [6]$$

1.2 Mechanisms of Quenching of Excited States by Oxygen

This reaction is thought to occur through a collision- cage recombination. The first step of a collision-cage recombination is the collision. The $Ru^{2+}*$ and oxygen molecule must encounter each other. [7, 8] Since Ru^{2+} is positive and O_2 is highly electronegative, an ion pair formation helps the molecules attract each other. This pairing-up of the molecules creates a type

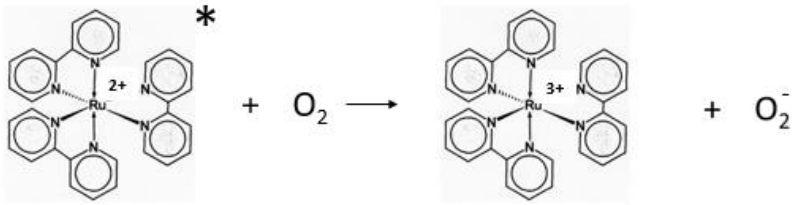
of cage that allows the electron to tunnel from $Ru^{2+}*$ to the oxygen molecule. However, the electron can also move back to the newly created Ru^{3+} from the O_2^- by means of recombination.

$$Ru^{2+*} + O_2 \rightleftharpoons Ru^{3+} + O_2^-$$

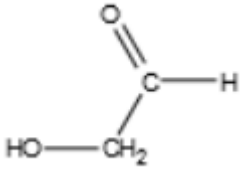


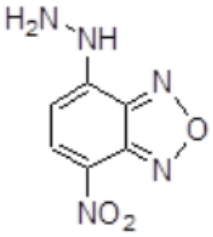
When looking at the efficiencies of charge separation, one must consider the back reaction. This recombination reaction is undesirable and give rise to no products. The idea is to separate the cage and dissociate before a recombination can occur. This dissociation traps the electron on the oxygen. The probability of this reaction happening fully with a successful transfer of the electron and dissociation is called the cage escape yield.

After oxidation with triethanolamine the final product eventually produces glycolic aldehyde. This reacts with 4-Hydrazino-7-nitro-2,1,3-benzoxadiazole (NBD-H) to form a flurescent hydrazine which can be detected and extracted with an organic solvent, in this case chlorobenzene. This reaction is shown on the next page.

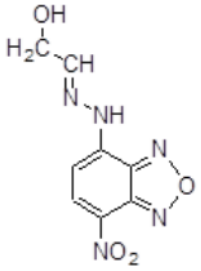


Triethanolamine





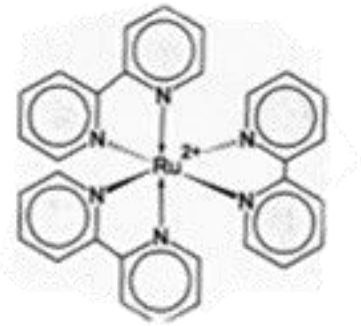
NBD-H



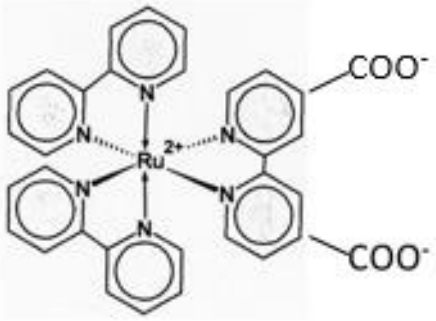
Fluorescent hydrazone

1.3 Statement of the Problem

The issue then becomes: how effective is this transfer of an electron? This experiment uses two complexes of Ru(2+): complex **1** tris(2,2'-bipyridine)ruthenium(II) and complex **2** bis(2,2'-bipyridine)(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II). The difference between the two molecules is the two carboxyl groups (COO^-) attached to each of the pyridines in one of the bipyridines in complex **2**. These complexes where choosen due to the strong metal-to-ligand charge transfer in the visible spectrum, as seen in figure 8 later in the paper. Ruthenium complexes have relatively long lifetimes for their excited state. This means there is a longer time, and higher chance for the desired Ru complex and oxygen reaction to occur. [9]



(**1**)



(**2**)

How does the coulombic interactions of the carboxylate functional groups contribute to the effectiveness of the reaction? This can be determined by comparing the quantum yield of product formation with the life times to obtain the efficiency of the charge separation.

1.4 Ru Complexes as Photosensitizers

This is important since $[Ru(bpy)_3]^{2+}$ can be used as a component of dye-sensitized solar cells, solar fuels catalysis, photoredox catalysis, the beginning of polymerization reactions and for photo-dynamic therapy. This is due to the unique ability of the complex to provide a radical ion intermediate in mild conditions. [10] This means such reactions can occur at room temperature with a commercial bulb instead of using high energy UV lights that are required to activate other radicals. This makes production safer, easier and more cost effective.

2. Experimental Techniques

2.1 Experimental Procedure

The samples are prepared a few days ahead of time. The reagent was freshly prepared at 4°C as a saturated solution of 4-Hydrazino-7-nitro-2,1,3-benzoxadiazole (NBD-H) in 10% by volume acetic acid. The photolyzing solution was created at the time of the experiment by placing 100 µL of 2M triethanolamine (TEOA), 890 µL of distilled water, and 10 µL of 10mMol Ru(II) complex in a small glass vial. A small magnetic stir-rod was placed in the vial as well and the solution was set to mix at a medium speed. While the solution was mixing, it was photolyzed with a 470 nm light diode for 30 second intervals, for up to 160 seconds. At every 30 second interval, 10 µL of the photolyzed solution was removed into a plastic cap. The 10 µL of the reagent was added to cap containing the photolyzed solution. This solution was set to react for approximately 5 minutes. After the solution was reacted, 200 µL of chlorobenzene was added to extract the desired product. This chlorobenzene was then extracted from the bottom of the cap and 160 µL was used to determine the emission intensity at 540 nm with a home-build emission spectrometer. That uses a silicon photodiode equipped with a interference filter. The photocurrent generated by the photodiode was read using an electrometer by Keithley Instruments.

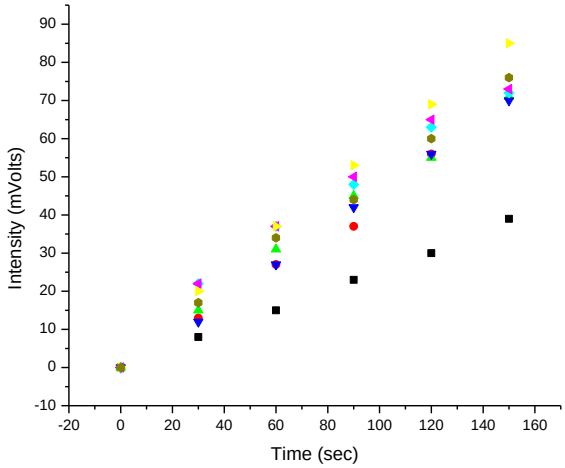


Figure 1: This is the graph of Intensity in mV verse Time in seconds. Each experimental trial is shown in a different color and has been set to start at the same zero point. The black squares are an outliar and have been excluded from data analysis.

2.1 Perfecting the Varibles

2.1.1 Time Limit

The time range was cut off after 160 seconds since light scattering and machine limitations causes the intensity to plateau after 160 seconds at around 275 mV. This limits the reaction due to emissions intensities to below 250 mV. This in turn limites photolyzing times to below 160 seconds.

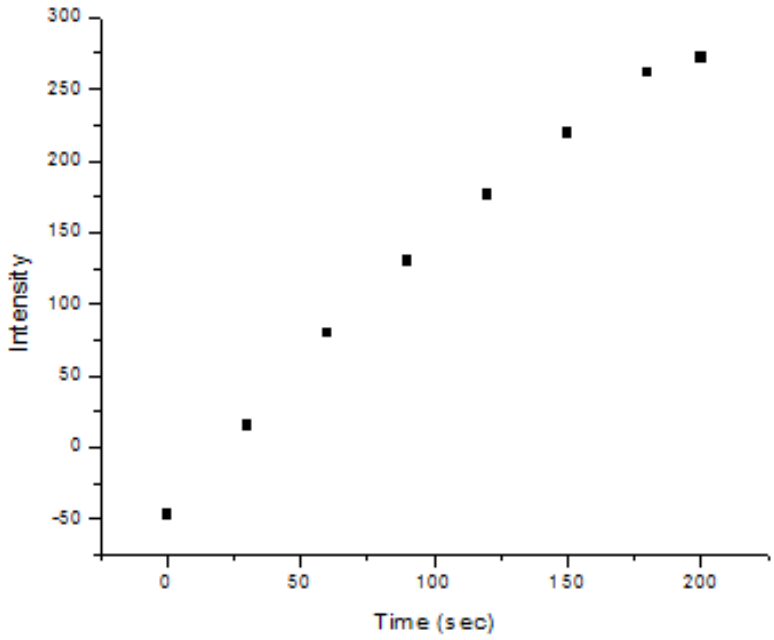


Figure 2: This is the graph of Intensity in mV verse Time in seconds for early trial runs inorder to determine a time limit for the experiment

2.1.2 Buffer Concentration

There is a dose dependence for product formation depending on the concentration of TEOA, which is used as the buffer in the photolyzed solution. To maximize the emission intensity, 0.2 M TEOA is used. As shown in the graph below, the emission intensity decreases with 0.1 M TEOA and there is no change in increased to 0.5 M TEOA. To use less material and solution, 0.2 M TEOA is used.

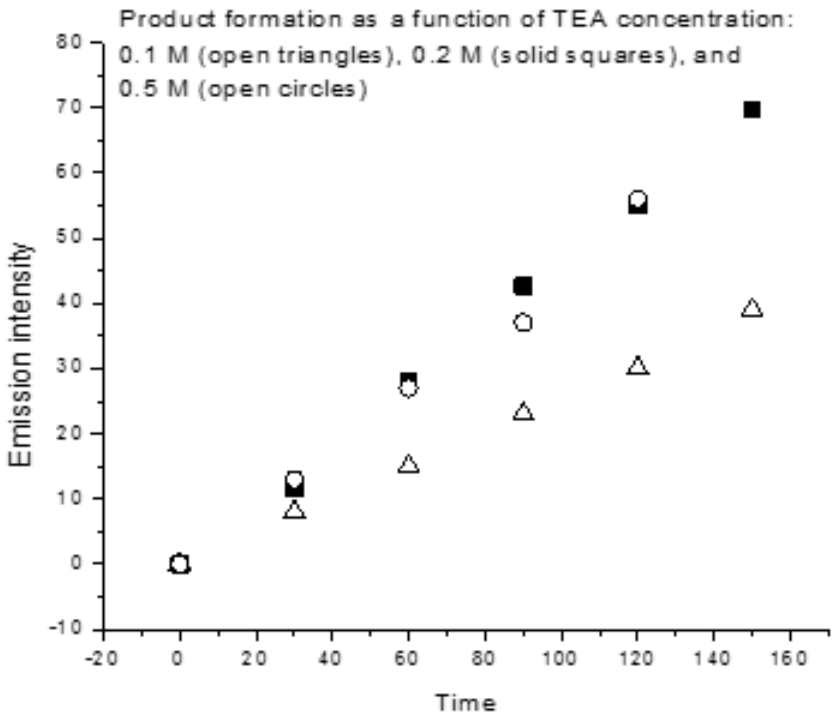


Figure 3: This graph shows the relation of TEOA concentrations with the formation of products. The open triangles are 0.1 M TEOA, the solid squares are 0.2 M TEOA and the open circles are 0.5 M TEOA

2.2 Light Intensity

The light intensity of the photolyzing diode must be determined. This is done using the very well-studied reaction of $K_3Fe^{III}(C_2O_4)_3$ into $Fe^{II}(Phen)_3^{2+}$ using a light wave under 500 nm using an actinometry method. This was done by using 1000 μL of 0.2M $K_3Fe^{III}(C_2O_4)_3$. The solution was illuminated for 30 second intervals for 120 seconds, removing 20 μL of the illuminated solution into 980 μL of the prepared buffer. The new solution was set in a dark area for approximately 30 minutes to react. The absorbance of the reacted solution was read at 510 nm. Knowing the quantum yield is 1.1 at 470 nm, combined with the path length of light being 1 cm and the molar extinction coefficient is $1.11*10^4 \frac{L}{mol*cm}$, the intensity of the diode can be determined.

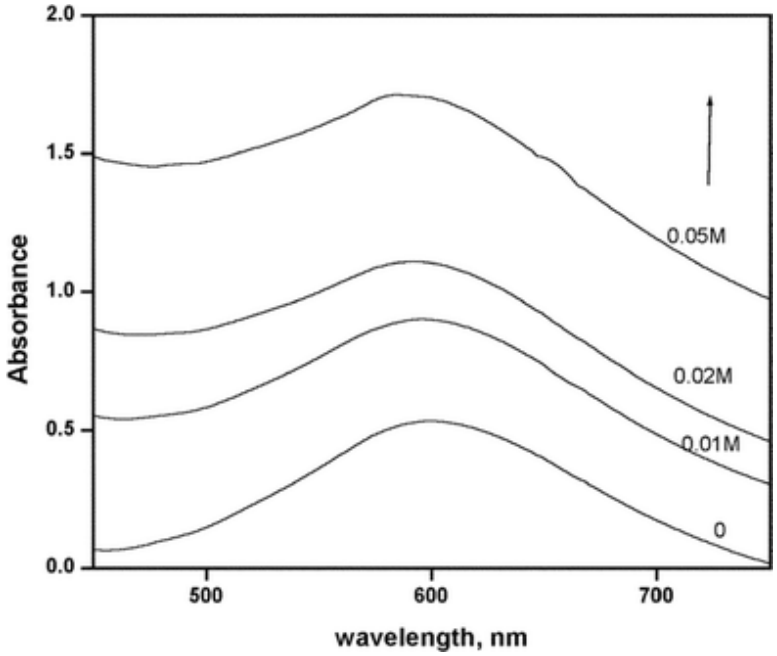


Figure 4: This is the intial UV-Spectra of into $Fe^{II}(Phen)_3^{2+}$ after different times. Each curve represent different concentration with the blank at the bottom and increasing upward with 0.01 M, 0.02M, and 0.05M.

Beer-Lambert's Law is used to relate absorbance to concetration: $A = \varepsilon lc$, where A is absorbance, ε is the the molar extinction coefficient, l is the length path of the light through the sample and c is the concentration. This allows the concentration to be solved for and after adding a dilution factor of x, it is given as $c = \frac{Ax}{\varepsilon l}$. The change of concentration over time is directly related to the change in absorbance over time: $\frac{dc}{dt} = \frac{x}{\varepsilon l} * \frac{dA}{dt}$. Once the change of absorbance over time is discovered, this information can be used to determine I using $\frac{dA}{dt} = I\phi\varepsilon lx$. This now allows the intial intensity of the light emitting diode to be determined using the correction factor $I = I_o(1 - 10^{-A})$, where A is the absorbance of the $K_3Fe^{III}(C_2O_4)_3$.

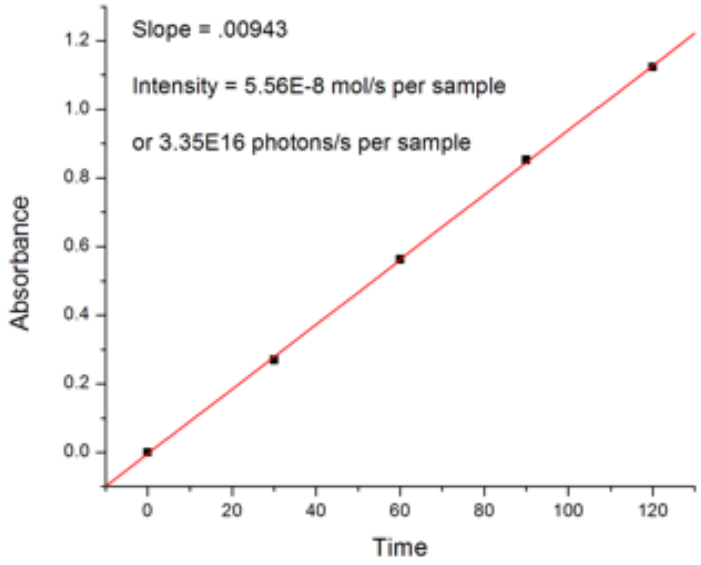


Figure 5: The absorbance at 470 nm was then plotted against time in seconds to find the slope of the line which represents the change in absorbance over time; $\frac{dA}{dt}$

2.3 Determining Concentration from Intensity

To turn the intensities gathered into concentrations in order to find the change in concentration over time, known concentrations of Ru(III) were treated the same with 0.2 M TEOA and reagent. The known concentrations of Ru(III) were formed by using a duliute Ru^{2+} complex by mixing 500 µL of distill water and 500 µL of 10 mM Ru^{2+}complex to form a solution of 5 mM Ru^{2+}complex. After the dilution, 3 µL of concentrated H_2SO_4 was added to create an acidic solution along with a small scoop of lead oxide. This forces the Ru^{2+} complex to react with the lead oxide to produce an Ru^{3+} complex in a known concentration of 5 mM. This gave a linear equation of [Ru(III)] = 5.02E-6*Int – 4.5E-5 mol/L for converting intensities to concentrations:

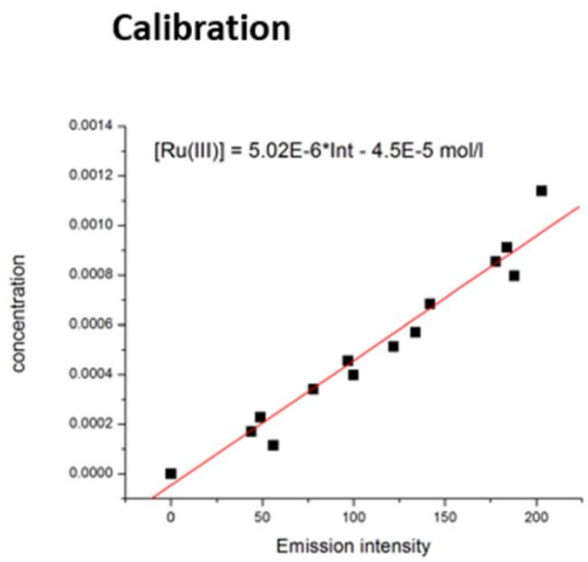


Figure 6: The emission intensity of known concentrations of Ru(III) give the following equation to turn emission intensities in to concentrations: [Ru(III)] = 5.02E-6*Int – 4.5E-5 mol/L

Using the data gathered, the intensities are turned into concentration, giving the following information.

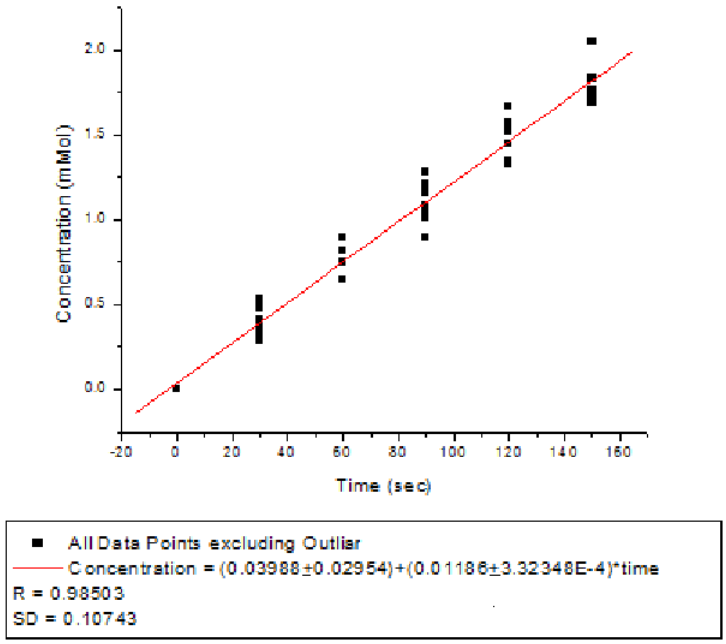


Figure 7: Experimental data after the emission intensities have been turned into concentrations. The slope of this graph give the change in concentration over time: $\frac{dc}{dt}$

3. Results

3.1 UV-Vis Spectra of Ru Complexes

The UltraViolet-Visible spectra of the Ru(II) complexes were taken using Varian 100 Spectrophotomer. It was found that the absorption maximum is around 470 nm. For complex **1**, the maximum absorbance is 0.968. For complex **2**, the maximum absorbance is 0.974. This is the A value for compounds which is needed for calculation of the quantum yield.

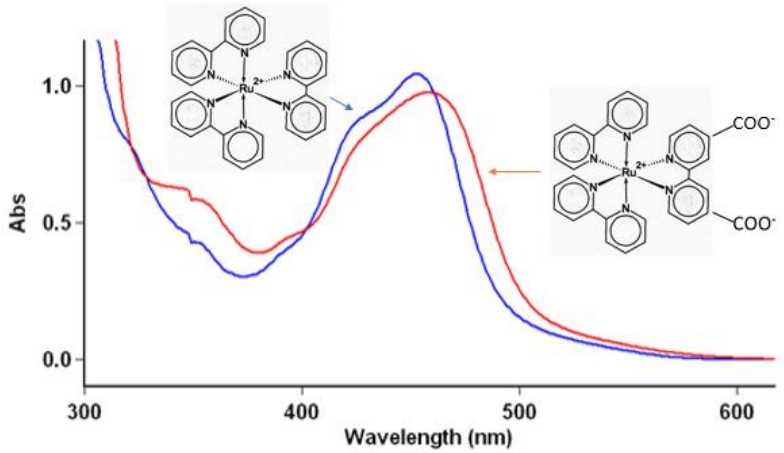


Figure 8: The UltraViolet-Visible spectra of the Ru(II) complexes. Complex **1** is shown in blue, while complex **2** is shown in red.

3.2 Product Fromation Dependence of Dose

Finally the product concentration is plotted against the dose to determine the quantum yield. The quantum yield is related to the amount of product formed per photon amount. The dose is simply the intensity of the light multiplied by the time the sample was exposed. The slope of this graph gives the quantum yield.

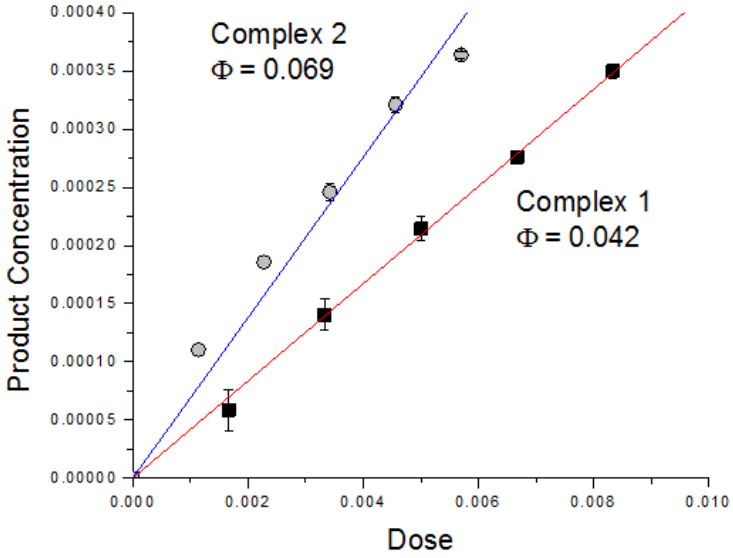


Figure 9: The product concentration as a function of dose for both complexes. Complex **1** is shown in red, while complex **2** is shown in blue.

4. Discussion & Conclusions

The table below best summarizes the results of this experiment. The yield (Y) can be found using α, which is fraction quenched by oxygen compared to competing reactions. α depends on two different lifetimes, denoted here as τ_o and τ. τ_o is the lifetimes with no oxygen present and τ is the lifetime in the presents of oxygen. [11]

Complex	**Φ**	**τ_o**	**τ**	**$\alpha = \frac{(\tau_o - \tau)}{\tau_o}$**	**$Y = \Phi/\alpha$**
1	0.042	570 ns	340 ns	0.40	**0.11**
2	0.069	480 ns	360 ns	0.25	**0.28**

It is shown here the the coulombic interactions between the quenching products significantly increases the yield of charge separation. This can be determined because of the carboxylate groups on complex **2** cause a larger coulombic interaction with the oxygen molecule, however, it has the higher yield. It can be postulated that the larger negative charge that the complex's ligands possess, the more likely the complex is to under go charge separation. The yield of charge separation is substantial, being over ten percent for complex **1** that only contains three bipyridine. However, the extra two negative charges from the carboxyl groups greatly increase the yield to twenty-five percent. This is a drastic increase of two hundred fifty percent.

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